CoZMo-POP

A Fugacity-Based Multi-Compartmental Mass Balance Model of the Fate of Persistent Organic Pollutants in the Coastal Zone

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1 Introduction and Motivation

CoZMo-POP (**Co**astal **Z**one **Mo**del for **P**ersistent **O**rganic **P**ollutants) is a non-steady state multi-media mass balance model for describing the long term fate of persistent organic pollutants (POPs) in a coastal environment or the drainage basin of a large lake. (Figure 1). The main focus is on quantifying environmental pathways, in particular the relative importance of the riverine and atmospheric pathway for delivering POPs to the aquatic ecosystem. Furthermore, the model aims to distinguish what fraction of the riverine load is atmospherically derived vs. being emitted directly to the soils, plants and rivers of a drainage basin.

The description of the drainage basin is restricted to those aspects which influence the magnitude and the timing of POPs delivery to the aquatic system. This implies that the model aims to describe accurately the rates of release (and the seasonal change of this release) of POPs from the main terrestrial storage media for POPs, i.e. soil and vegetation, into the two transport media delivering POPs to the aquatic environment, i.e. atmosphere and fresh water. Vegetation and soil have to be treated separately, if their characteristics of exchange with the atmosphere are different. This is the case for forests which display much faster uptake for many POPs than grassland and fields planted with agricultural crops.

Key processes are the two-directional exchange, or cycling, of POPs between the atmosphere and aquatic and terrestrial surfaces, and the uni-directional run-off of chemical from soil to fresh water and further to the marine system. Important are further the processes that could lead to loss of chemical during the transport in atmosphere and river water, i.e. degradation and deposition in the atmosphere, and degradation, net sedimentation to fresh water sediments, and volatilisation in the fresh water system.
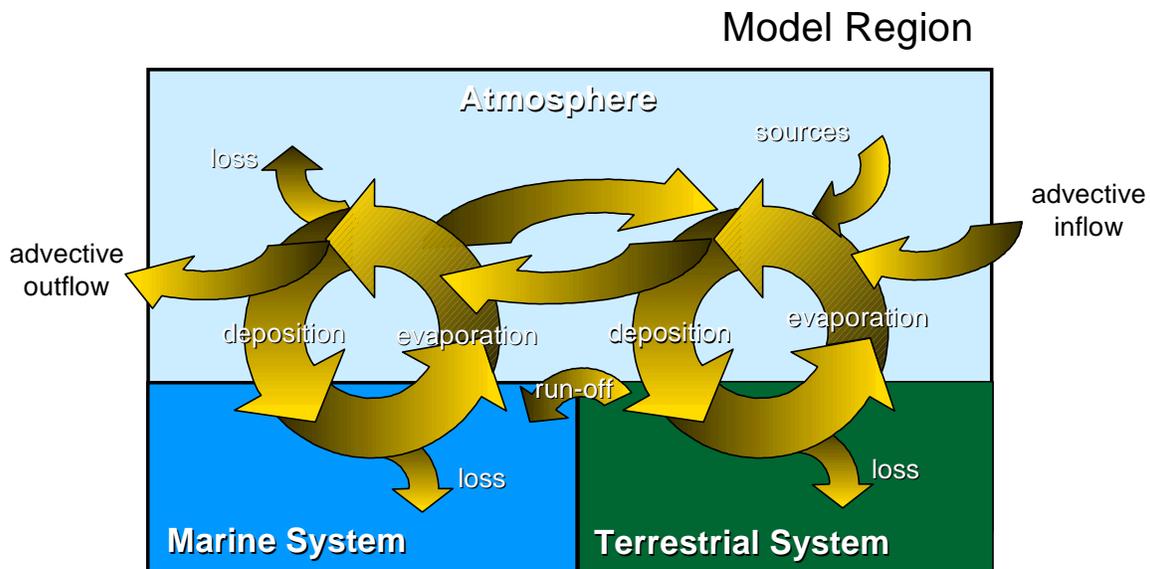

Figure 1   CoZMo-POP aims to quantify the pathways of POPs from the terrestrial environment to the marine environment via atmosphere and rivers.

2 System Boundary and Compartments in CoZMo-POP

The modelled system comprises a coastal water body (or lake) and its entire drainage basin, including the troposphere above this region. This is a deviation from most previous models of large water bodies which tend to be restricted to the aquatic environment. In aquatic models the air-water interface and the river mouths constitute system boundaries and riverine inflow concentrations and atmospheric concentrations over the water surface are model input parameters supplied by the user (Figure 2).

This neglects the possibility of interactions between the water body, the atmosphere above it and its drainage basin. It is well established that atmospheric concentrations of many POPs are governed by the exchange with the Earth's surface, and it is conceivable that a large water body can act as a supply of persistent chemicals to its terrestrial surroundings and vice versa. Atmospheric and riverine concentrations therefore should be calculated by the model rather than being supplied as input parameters. This aspect of the model reflects a trend within water quality modelling to progressively include more parts of the overall system within the system boundaries (Thomann, 1998).
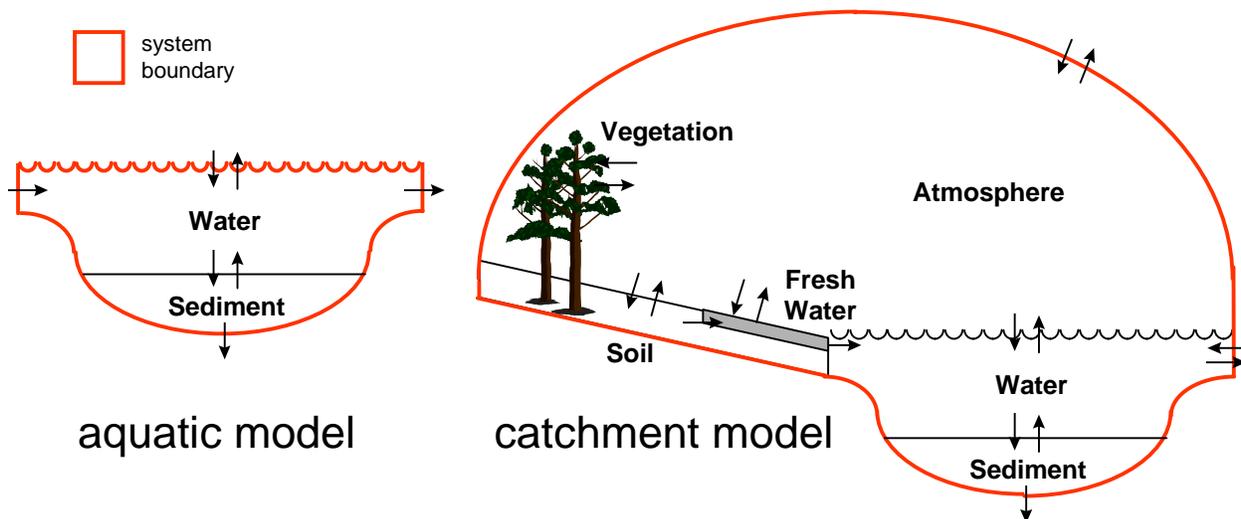

Figure 2   The system of a catchment model includes the drainage basin of the water body and the atmosphere above it.

A typical multi-media mass balance model divides the environment into a number of boxes or compartments, which are considered well-mixed and homogeneous, with respect to both environmental characteristics and chemical contamination. These environmental phases are then linked by a variety of intercompartmental transfer processes. CoZMo-POP consists of eight such boxes or compartments: atmosphere (A), forest canopy (F), forest soil (B), agricultural soil (E), fresh water (W), fresh water sediment (S), coastal water (C), and coastal sediment (L). Figure 3 shows all the compartment types and how they are interconnected.
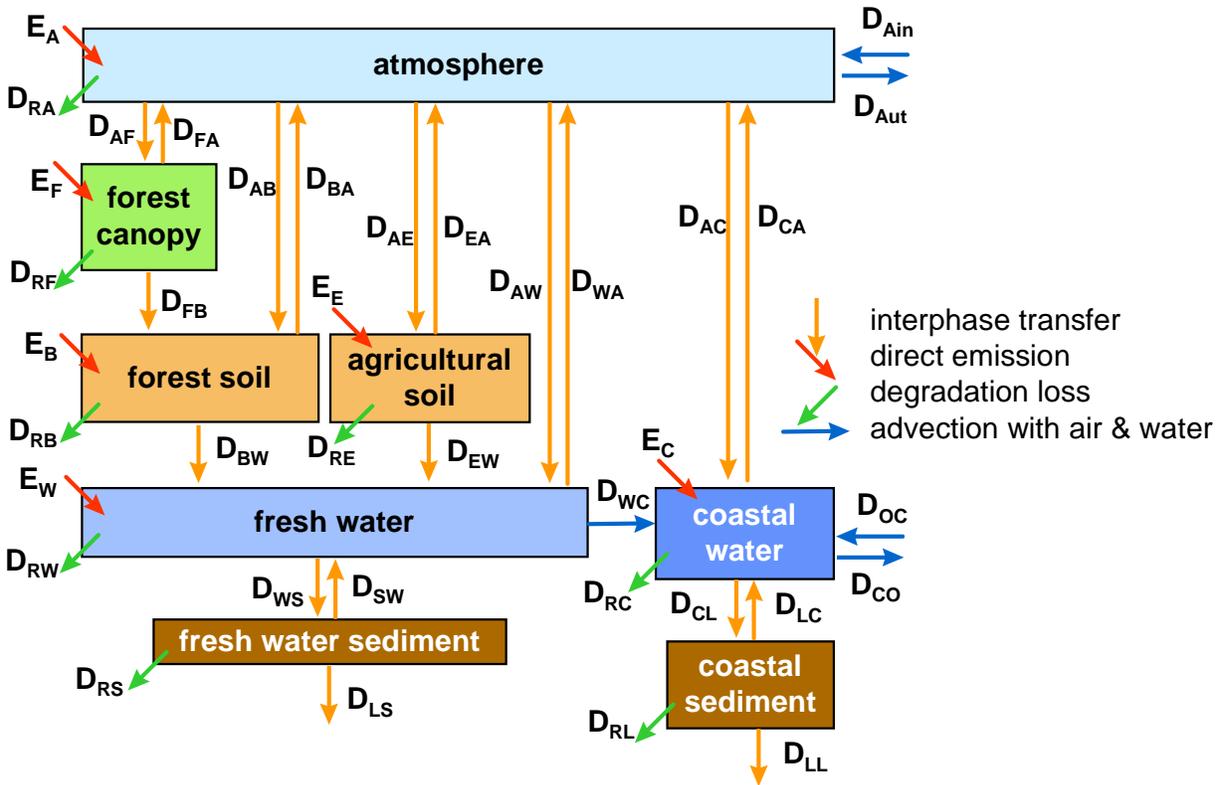
Figure 3   Schematic representation of the environmental compartments and contaminant fate processes in CoZMo-POP.

3 Description of the Natural Environment in CoZMo-POP

The movement of POPs in the environment is closely associated with the movement of air, water and particulate organic carbon (POC). In CoZMo-POP advective intercompartmental transfer fluxes for the contaminants are calculated as the product of a flux of a carrier phase, namely air, water and POC (in units of volume per time) and a contaminant concentration in that phase (in units of moles per volume). Solving the mass balance for the contaminants thus requires the construction of mass balances for air, water and POC within the modelled system.

Mass Balance of Air. The rate of advection of air in and out of the model region aG is calculated from the volume of the atmospheric compartment, which is the product of the total surface area ($A_C + A_B + A_E + A_W$) and the atmospheric height h_A, and the user-specified atmospheric residence time t_A.

Mass Balance for Water. A complete steady-state water balance is formulated for the model region (Figure 4). The water input to a compartment by precipitation is estimated from user-defined rain rates for the terrestrial environment U_{3T} and the coastal basin U_{3C}, and the compartmental surface areas A_X. It is assumed that all water is intercepted by the forest canopy, and no rain falls directly to the forest soil. Evaporation loss is estimated employing user-defined fractions frU_X of the total water flow to a compartment X that evaporates from that compartment. The intercompartmental water fluxes are then derived as the balance of input by precipitation and run-off and loss by evaporation (Table 1). The model neglects the seasonality of precipitation input, evaporation intensity and riverine run-off.
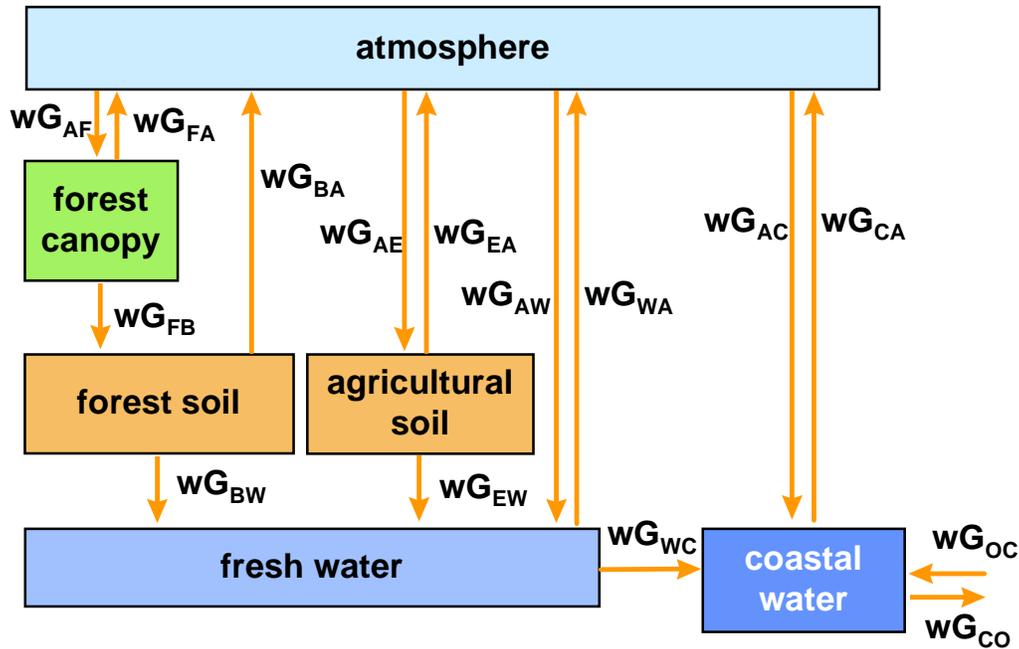
Figure 4 Water fluxes between the compartments of CoZMo-POP.

Table 1 Equations used to calculate the fluxes of water between the various model compartments

precipitation to forest canopy

$wG_{AF} = U_{3T} \cdot A_B$

through fall and stem flow

$wG_{FB} = (1 - frU_F) \cdot wG_{AF}$

precipitation to agricultural soil

$wG_{AE} = U_{3T} \cdot A_E$

run-off/leaching from forest soil to fresh water

$wG_{BW} = (1 - frU_B) \cdot wG_{FB}$

precipitation to fresh water system

$wG_{AW} = U_{3T} \cdot A_W$

run-off from the fresh water to coastal water

$wG_{WC} = (1 - frU_W) \cdot (wG_{BW} + wG_{EW} + wG_{AW})$

precipitation to the coastal water

$wG_{AC} = A_C \cdot U_{3C}$

net flow of water between coastal and open water

$wG_{CO} = (1 - frU_C) \cdot (wG_{WC} + wG_{AC}) \cdot (1 + facGF)$

evaporation from forest canopy

$wG_{FA} = frU_F \cdot wG_{AF}$

evaporation from forest soil

$wG_{BA} = frU_B \cdot wG_{FB}$

evaporation from agricultural soil

$wG_{EA} = frU_E \cdot wG_{AE}$

run-off/leaching from agri-soil to fresh water

$wG_{EW} = (1 - frU_E) \cdot wG_{AE}$

evaporation from fresh water

$wG_{WA} = frU_W \cdot (wG_{BW} + wG_{EW} + wG_{AW})$

evaporation from coastal water

$wG_{CA} = frU_C \cdot (wG_{WC} + wG_{AC})$

$wG_{OC} = (1 - frU_C) \cdot (wG_{WC} + wG_{AC}) \cdot facGF$

Mass Balance for Particulate Organic Carbon. Both within the terrestrial and aquatic environment, POPs attach themselves preferentially to organic material, and the advective fluxes of the contaminants between virtually all compartments include advection with organic matter. In fact, for POPs, which typically have a log K_{OW} greater than 4, attachment to organic matter tends to be so much stronger than to mineral surfaces, that the latter can be neglected. In CoZMo-POP advective fluxes of particulate organic carbon (POC) between compartments (in units of m³/h) are derived to calculate the advective transport of POPs with POC. Explicitly required to calculate contaminant fluxes are the run-off of POC from soils to fresh water and from fresh to coastal water, the advection of POC between coastal water and open sea, and the POC sedimentation, resuspension and burial fluxes in the fresh and coastal water bodies. For the calculation of phase partitioning, additionally concentrations of POC in the water phase and fractions of organic carbon in the sediment particles are required. To assure that the values for these fluxes and concentrations are internally consistent, a complete POC mass budget for the aquatic system is constructed in CoZMo-POP (Figure 5). These budgets include rates of primary production and POC mineralisation even though they are not required for the contaminant mass balance. Input parameters for construction of these mass budgets are:

- the water fluxes wG_{EW}, wG_{BW}, wG_{WC}, wG_{CO}, and wG_{OC} derived in the previous section

- the concentration of POC in fresh and coastal water, $Cpoc_W$ and $Cpoc_C$ in units of mg/L.

- the mass fraction POC in fresh water and coastal sediment solids, OC_W and OC_C in g C/g sediment solids

- the primary productivities in fresh and coastal water, $BP_{W/C}$ and $BP_{W/C}$ in g POC / (m³·a)

- the fractions of the total net input of POC to water column, which is mineralised in the water column, $facO_{Wmiw}$ and $facO_{Cmiw}$

- the fractions of the POC deposited to the sediments, which is resuspended, $facO_{Wres}$ and $facO_{Cres}$

- the fraction of the POC net-deposited (oG_{sed} - oG_{res}) that is mineralised in the surface sediment, $facO_{Wmis}$ and $facO_{Cmis}$

- the volume fraction of solids in water running-off from soils, VF_{SB} and VF_{SE} and the volume fraction of POC in these solids, VF_{OB} and VF_{OE}.

The volume fractions of organic carbon in soil particles are calculated from the organic carbon mass fractions OC_X using:

$VF_{OE} = 1 / (1 + ((1 - OC_E) \cdot \delta_{OC} / (OC_E \cdot \delta_{MM})))$

$VF_{OB} = 1 / (1 + ((1 - OC_B) \cdot \delta_{OC} / (OC_B \cdot \delta_{MM})))$

The POC fluxes are derived using the equations given in Table 2. The calculation of oG_{WC} may require some explanation. Much of the organic carbon in rivers is dissolved organic carbon (DOC). Upon mixing with saline waters, part of this DOC flocculates to form POC. It is assumed that on average (1) riverine POC concentrations are 10 times lower than DOC concentration and (2) 25 % of the riverine DOC load flocculates into POC in the coastal zone, the latter based on studies by Forsgren and Jansson (1992). This elevated oG_{WC} is only calculated as input to the POC balance for the coastal compartments. The advective transport of POPs sorbed to carbon from the fresh water to the coastal water compartment is only based on the transport of riverine POC.
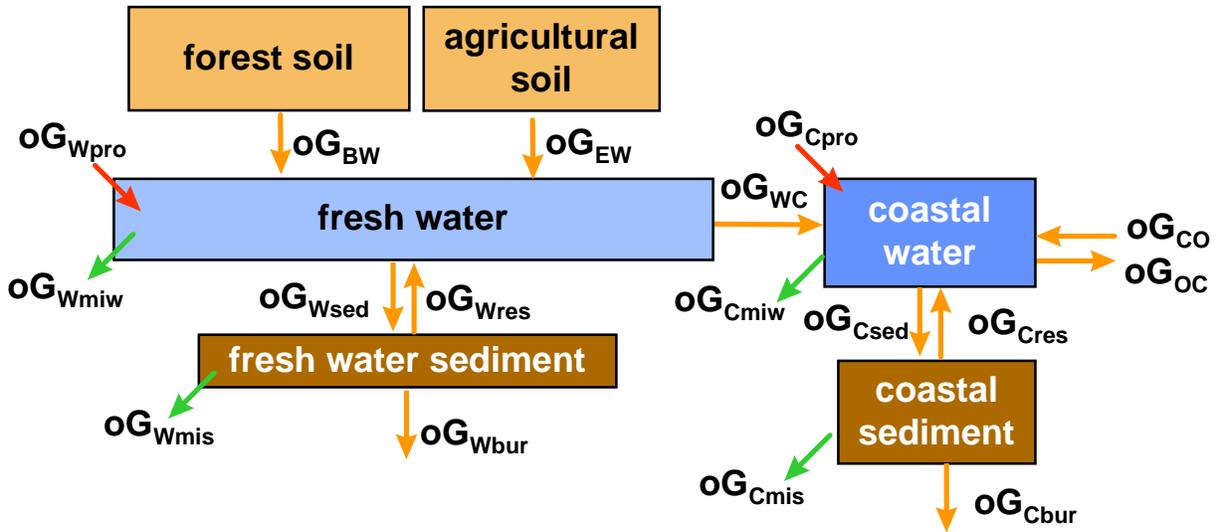
Figure 5 A particulate organic carbon mass balance is constructed for the aquatic system.

Table 2 Equations used to construct the POC mass budgets in the aquatic environments.

Inflow from soils to fresh water

$oG_{BW} = wG_{BW} \cdot VF_{SB} \cdot VF_{OB}$ $\qquad oG_{EW} = wG_{EW} \cdot VF_{SE} \cdot VF_{OE}$

POC inflow to coastal waters with rivers

$oG_{Criv} = wG_{WC} \cdot 3.5 \cdot Cpoc_W / \delta_{OC}$

advection of POC between coastal water and the open sea

$oG_{OC} = (G_{OC} \cdot Cpoc_O) / \delta_{OC}$ $\qquad oG_{CO} = (G_{CO} \cdot Cpoc_C) / \delta_{OC}$

Primary production of POC

$oG_{Wpro} = (BP_W / 8760) \cdot A_W / \delta_{OC}$ $\qquad oG_{Cpro} = (BP_C / 8760) \cdot A_C / \delta_{OC}$

Mineralisation of POC in the water column

$oG_{Wmiw} = oG_{Wintot} \cdot facO_{Wmiw}$ $\qquad$ where $oG_{Wintot} = oG_{Wpro} + oG_{BW} + oG_{EW} - oG_{WC}$

$oG_{Cmiw} = oG_{Cintot} \cdot facO_{Cmiw}$ $\qquad$ where $oG_{Cintot} = oG_{Cpro} + oG_{WC} + oG_{OC} - oG_{CO}$

POC resuspension rate

$oG_{Wres} = (oG_{Wintot} - oG_{Wmiw}) / (1 / facO_{Wres} - 1)$ $\qquad oG_{Cres} = (oG_{Cintot} - oG_{Cmiw}) / (1 / facO_{Cres} - 1)$

POC deposition rate

$oG_{Wsed} = oG_{Wres} / facO_{Wres}$ $\qquad oG_{Csed} = oG_{Cres} / facO_{Cres}$

Mineralisation rate of POC in the surface sediment

$oG_{Wmis} = facO_{Wmis} \cdot (oG_{Wsed} - oG_{Wres})$ $\qquad oG_{Cmis} = facO_{Cmis} \cdot (oG_{Csed} - oG_{Cres})$

POC burial rate in sediments

$oG_{Wbur} = oG_{Wintot} - oG_{Wmiw} - oG_{Wmis}$ $\qquad oG_{Cbur} = oG_{Cintot} - oG_{Cmiw} - oG_{Cmis}$

Other Organic Carbon fluxes. Organic matter is also "advected" between the atmosphere and the Earth's surface in the form of organic aerosol and between the forest canopy and the forest soil in the form of falling leaves. In these cases no explicit particulate organic carbon fluxes are derived in the model. The flux of POPs associated with organic matter is handled differently in the model, and organic carbon fluxes are only involved implicitly. By calculating the Z-value of aerosols using a relationship with the octanol-air partition coefficient K_{OA}, we assume that aerosols consist of a certain fraction organic matter, that has similar partitioning properties as n-octanol (Finizio et al. 1998). No explicit fraction organic matter can be derived from that relationship, because it is empirical. In addition to the organic matter fraction, the relationship is dependent on the partitioning properties of the organic matter relative to those of octanol. Fluxes to the surface are calculated using particle scavenging ratios and dry deposition velocities. Advection between canopy and forest soil is described using advective fluxes on a whole leaf basis rather than a organic carbon basis. The advective flux of leaves/needles G_{FB} has units of m^3 leaves/h.

Temperatures. One of the most important environmental parameters with influence on the behaviour of POPs in the environment is temperature. In CoZMo-POP different temperatures are defined for the atmosphere T_A, the terrestrial environment T_T, and the coastal environment T_C. T_A is used to calculated the partitioning between gas phase and particles, and the degradation rate in the atmosphere. Atmosphere-surface exchange is assumed to take place at the temperature of the surface compartment. The fresh water environment T_W adopts the temperature of the terrestrial environment T_T, except that the temperature does not drop below -2 °C.

Forest Volume and Composition. The volume of foliage in a temperate forest changes through the seasons, particularly for deciduous forests. In the model the volume of the coniferous canopy V_{Fcon} is assumed to increase slightly throughout spring and summer, and decline during the rest of the year (the annual growth matches the annual loss by needle fall), whereas the deciduous forest canopy volume V_{Fdec} is assumed to increase quickly during spring, to be constant during summer, to decrease rapidly in autumn as the leaves fall, and to stay constant at a fraction frc_{Leaf} of the summer value during winter (Figure 6). V_{Fcon} and V_{Fdec} in m^3 are calculated as products of specific canopy volumes per ground area, sV_{Fcon} and sV_{Fdec} in m^3/m^2 and the forest soil surface area A_B. The volume of the mixed canopy V_F is calculated using a factor Φ_{con}, which defines what fraction of the forest is made up of coniferous trees:

$$V_F = V_{Fcon} \cdot \Phi_{con} + V_{Fdec} \cdot (1 - \Phi_{con})$$

A seasonally changing volume fraction of coniferous canopy in the total canopy v_{conF}, which is needed for determining the bulk Z-value of the forest canopy, is calculated as well:

$$v_{conF} = (V_{Fcon} \cdot \Phi_{con}) / V_F$$

Litter Fall. Transport of chemical from the canopy to the soil is assumed to occur by litter fall only, neglecting the leaching of organic material from the canopy (Horstmann and McLachlan, 1996). This advective transport is described defining a litter fall rate G_{FB} in units of m^3 "canopy" per h. Whereas G_{FB} in a coniferous forest is more or less continuous, in a deciduous forest there is a short pulse connected with the shedding of leaves in the fall. Needles are assumed to fall at a constant rate throughout the year, determined by the average time a needle stays on the tree t_{Needle}. For a deciduous canopy it is assumed that all of the litter fall occurs in the fall at a constant rate (Figure 6). This rate is calculated from the difference in deciduous canopy volume between summer and winter, maintaining the "leaf mass balance".
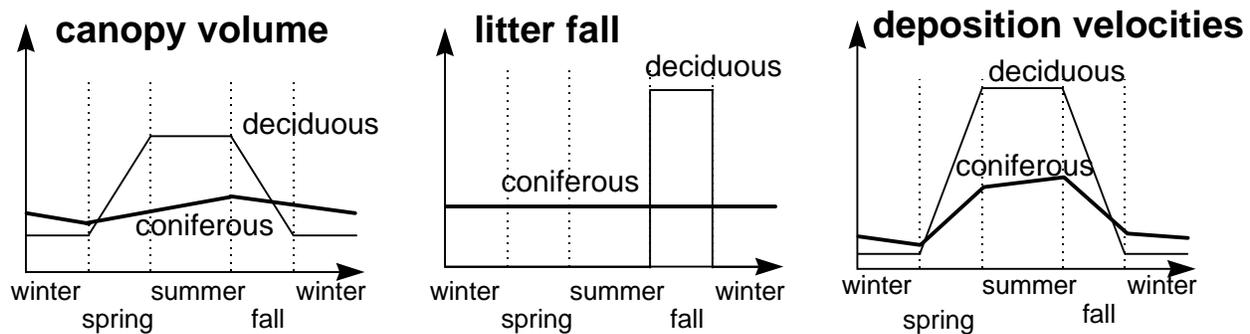
Figure 6   Schematic representation of the seasonal dependence of the volume of the forest canopy V_F, the litter fall advection term G_{FB}, and of the deposition velocities to the forest canopy v_D. During winter, summer average, i.e. maximum, values for v_D are reduced by a factor describing the relative stability of the atmosphere. Spring and fall values are derived from linear interpolation between summer and winter values.

4 Description of Contaminant Fate in CoZMo-POP

The mass balance equations for the contaminant (Table 3) are formulated in terms of fugacity, i.e. employ the concepts of Z-values to describe phase partitioning and D-values to describe contaminant fate processes (Mackay, 1991). The expressions for phase partitioning, intermedia transport and degradation are building upon those from previous fugacity models. The description of contaminant fate processes in the aquatic environment is similar to that in a model of POP fate in the Baltic Sea (Wania et al., 2000), whereas the description of the contaminant fate processes in the drainage basin is similar to that used in the Global Distribution Model (Wania and Mackay, 1995). These models trace their origin to older models, namely the generic model by Mackay et al. (1992) and the QWASI model (Mackay et al., 1983). There are however, significant modifications:

1. Most significantly, the description of the terrestrial environment includes a forest canopy compartment, and thus several novel fate processes such as atmosphere-canopy and canopy-forest soil exchange.

2. The mass transfer coefficient from the soil to the soil surface is assumed to have a lower threshold to account for the impact of physical soil mixing processes such as bioturbation and ploughing on the mobility of highly sorptive SOCs in soil.

3. Gas-particle partitioning in the atmosphere is calculated with a K_{OA}-based approach instead of the classical Junge-Pankow model, because this eliminates the need to specify a contaminant vapour pressure.

4. The mass transfer coefficient for diffusive exchange across the sediment-water interface distinguishes between molecular diffusion in the water-filled pore space and bioturbative mixing.

5. Mass transfer coefficients for air-water exchange are calculated from seasonally variable wind speed.

6. Deposition velocities to the terrestrial compartments are modified by a factor describing the seasonally variable stability of the atmosphere.

7. All fate processes are described as a function of seasonally variable temperature.

In the following, details are provided for how the various Z and D-values in Table 3 are being calculated in CoZMo-POP.

Table 3   The mass balance equations over the eight compartments of CoZMo-POP.

Atmospheric Compartment

$dM_A/dt = d(V_A \cdot BZ_A \cdot f_A)/dt = E_A + D_{FA} \cdot f_F + D_{BA} \cdot f_B + D_{EA} \cdot f_E + D_{WA} \cdot f_W + D_{CA} \cdot f_C + D_{Ain} \cdot f_{Aut} - f_A \cdot (D_{RA} + D_{AF} + D_{AB} + D_{AE} + D_{AW} + D_{AC} + D_{Aut})$

Forest Canopy Compartment

$dM_F/dt = d(V_F \cdot BZ_F \cdot f_F)/dt = E_F + D_{AF} \cdot f_A - f_F \cdot (D_{RF} + D_{FA} + D_{FB})$

Forest Soil Compartment

$dM_B/dt = d(V_B \cdot BZ_B \cdot f_B)/dt = E_B + D_{AB} \cdot f_A + D_{FB} \cdot f_F - f_B \cdot (D_{RB} + D_{BA} + D_{BW})$

Agricultural Soil Compartment

$dM_E/dt = d(V_E \cdot BZ_E \cdot f_E)/dt = E_E + D_{AE} \cdot f_A - f_E \cdot (D_{RE} + D_{EA} + D_{EW})$

Fresh Water Compartment

$dM_W/dt = d(V_W \cdot BZ_W \cdot f_W)/dt = E_W + D_{AW} \cdot f_A + D_{BW} \cdot f_B + D_{EW} \cdot f_E + D_{SW} \cdot f_S - f_W \cdot (D_{RW} + D_{WA} + D_{WC} + D_{WS})$

Fresh Water Sediment Compartment

$dM_S/dt = d(V_S \cdot BZ_S \cdot f_S)/dt = D_{WS} \cdot f_W - f_S \cdot (D_{RS} + D_{LS} + D_{SW})$

Coastal Water Compartment

$dM_C/dt = d(V_C \cdot BZ_C \cdot f_C)/dt = E_C + D_{AC} \cdot f_A + D_{WC} \cdot f_W + D_{LC} \cdot f_L + D_{OC} \cdot f_O - f_C \cdot (D_{RC} + D_{CL} + D_{CA} + D_{CO})$

Coastal Sediment Compartment

$dM_L/dt = d(V_L \cdot BZ_L \cdot f_L)/dt = D_{CL} \cdot f_C - f_L \cdot (D_{RL} + D_{LL} + D_{LC})$

4.1 Description of Phase Partitioning in CoZMo-POP

As is typical for fugacity based models, equilibrium phase partitioning in CoZMo-POP is expressed in terms of Z-values or fugacity capacities. Each compartment has a contaminant specific Z-value expressing its capacity to hold chemical for a certain rise in fugacity. Z-values are typically calculated from equilibrium partition coefficients. Pure phase Z-values are calculated for air Z_A, water Z_W and particulate organic carbon Z_{POC}. Because Z-value are temperature dependent and different temperatures are specified for the atmospheric, the terrestrial, and the coastal water compartment, several Z-values for water, air and POC have to be calculated. Also, the Z-values are time-variant, a result of seasonally changing temperature values. The Z-values for the bulk compartments, or bulk Z-values BZ_X are weighted fractions of the pure phase Z-values, the weights being the volume fractions of the various sub-phases making up a compartment.

4.1.1 Phase Partitioning in the Atmosphere

The Z-values for the pure air and water phase at the atmospheric temperature are calculated from atmospheric temperature T_A and Henry's law constant H, respectively:

$Z_A(T_A) = 1 / (R \cdot T_A)$

$Z_W(T_A) = 1 / H(T_A)$

In the case of particulate organic matter in the atmosphere, no Z_{POC} is calculated, but rather a Z-value for the entire aerosol Z_Q. This Z_Q is based on empirically derived regressions between measured air-particle partition coefficients and the octanol-air partition coefficient K_{OA}.

$Z_Q = M_Q \cdot K_{OA}^{NQ} \cdot Z_A(T_T) = M_Q \cdot K_{OA}^{NQ} / (R \cdot T_T)$

The default regression parameters of $M_Q = 3.5$ and $N_Q = 1$ are based on Finizio et al. (1997).

Bulk Z-values for the dry atmosphere are derived using volume fractions of solids in air VF_{SA}:

atmosphere inside model region $\qquad BZ_A = Z_A(T_A) + VF_{SA} \cdot Z_Q$

air advected into the model region $\qquad BZ_{Aut} = Z_A(T_A) + VF_{SAut} \cdot Z_Q$

A Z-value for rain close to the earth's surface is calculated using:

$BZ_{RAIN} = Z_W(T_A) + Q \cdot VF_{SA} \cdot Z_Q$

where Q is the particle scavenging ratio.

4.1.2 Phase Partitioning in the Aqueous Systems

Z-values for air, water and particulate organic carbon at the temperatures of the fresh and coastal water system T_W and T_C are calculated using:

$Z_A(T_W) = 1 / (R \cdot T_W)$ $\qquad\qquad Z_A(T_C) = 1 / (R \cdot T_C)$

$Z_W(T_W) = 1 / H(T_W)$ $\qquad\qquad Z_W(T_C) = 1 / H(T_C)$

$Z_{POC}(T_W) = Z_W(T_W) \cdot K_{POC}$ $\qquad\qquad Z_{POC}(T_C) = Z_W(T_C) \cdot K_{POC}$

The partition coefficient between particulate organic carbon and water K_{POC} is derived from empirical regressions with the octanol-water partition coefficient K_{OW}

$K_{POC} = M_{POC} \cdot K_{OW}$

Typical values for the empirical parameter M_{POC} are 0.35 (Seth et al., 1999) and 0.41 (Karickhoff et al., 1981). The model allows for different M_{POC} in fresh water and coastal water.

Using the concentrations of POC in the water column a bulk Z-values for water is derived:

fresh water $\qquad\qquad\qquad\qquad BZ_W = Z_W(T_W) + (Cpoc_W / \delta_{OC}) \cdot Z_{POC}(T_W)$

coastal water $\qquad\qquad\qquad\qquad BZ_C = Z_W(T_C) + (Cpoc_C / \delta_{OC}) \cdot Z_{POC}(T_C)$

water flowing in from open sea $\qquad BZ_O = Z_W(T_C) + (Cpoc_O / \delta_{OC}) \cdot Z_{POC}(T_C)$

In sediments only water and particulate organic carbon are assumed to contribute to the fugacity capacity:

$BZ_S = (1 - VF_{SS}) \cdot Z_W(T_W) + VF_{SS} \cdot VF_{OS} \cdot Z_{POC}(T_W)$

$BZ_L = (1 - VF_{SL}) \cdot Z_W(T_C) + VF_{SL} \cdot VF_{OL} \cdot Z_{POC}(T_C)$

4.1.3 Phase Partitioning in the Soil System

Z-values for air, water and organic carbon at the temperature of the terrestrial environment T_T are:

$Z_A(T_T) = 1 / (R \cdot T_T)$

$Z_W(T_T) = 1 / H(T_T)$

$Z_{POC}(T_T) = Z_W(T_T) \cdot K_{POC}$

K_{POC} for soil organic carbon is derived in an identical fashion to the POC in the aquatic system, with soil specific regression parameters M_{POC}.

Bulk Z-value for soils are calculated using the volume fractions of air, water and POC:

$BZ_E = VF_{WE} \cdot Z_W(T_T) + VF_{AE} \cdot Z_A(T_T) + (1 - VF_{WE} - VF_{AE}) \cdot VF_{OE} \cdot Z_{POC}(T_T)$

$BZ_B = VF_{WB} \cdot Z_W(T_T) + VF_{AB} \cdot Z_A(T_T) + (1 - VF_{WB} - VF_{AB}) \cdot VF_{OB} \cdot Z_{POC}(T_T)$

4.1.4 Z-value for the Forest Canopy

A fugacity capacity of the forest canopy compartment Z_F is calculated from a foliage-air partition coefficient K_{FA} which in turn is determined from empirical regressions of measured K_{FA}s against the octanol-air partition coefficient K_{OA} (Horstmann and McLachlan, 1998).

$Z_F = K_{FA} \cdot Z_A(T_T) = K_{FA} / (R \cdot T_T) = (M_F \cdot K_{OA}{}^{NF}) / (R \cdot T_T)$

Because the empirical coefficients M_F and N_F differ for a deciduous and a coniferous canopy, two Z-values Z_{Fdec} and Z_{Fcon} are calculated. The bulk Z-value of the forest canopy BZ_F consisting of coniferous and deciduous trees is calculated using a volume fraction of coniferous leaves in the forest canopy v_{conF}, which is a time variant parameter (see above):

$BZ_F = (1 - v_{conF}) \cdot Z_{Fdec} + v_{conF} \cdot Z_{Fcon}$

4.2 Description of Chemical Fate Processes in CoZMo-POP

Transport and degradation processes in fugacity-based models are described with the help of D-values in units of mol/(Pa·h) (Mackay, 1991). There are principally three types of processes:

- advective transport processes
- diffusive transport processes, and
- degradation processes.

4.2.1 Description of Advective Processes

D-values for the transport of contaminant with advected air, water and POC are expressed as the product of the transfer rate of the carrier medium xG in units of m^3/h and its Z-value in units of mol/(m^3·Pa) (Mackay, 1991).

DESCRIPTION OF ATMOSPHERIC ADVECTION

The bulk air Z-values are multiplied with the atmospheric advection rate aG to give atmospheric advection D-value for the exchange with the atmosphere outside of the model boundaries.

$D_{Aut} = BZ_A \cdot aG$ $D_{Ain} = BZ_{Aut} \cdot aG$

DESCRIPTION OF ADVECTION IN WATER

The same approach is used for the run-off from fresh water to coastal water D_{WC}, and the exchange between the marine compartments D_{CO}, D_{OC}:

$D_{WC} = BZ_W \cdot wG_{WC}$ $D_{CO} = BZ_C \cdot wG_{CO}$ $D_{OC} = BZ_O \cdot wG_{OC}$

DESCRIPTION OF SOIL-FRESH WATER EXCHANGE

The run-off from soil to fresh water is calculated as the sum of contaminant advected with run-off water and contaminant advected with eroded particulate organic matter.

$$D_{EW} = wG_{EW} \cdot Z_W(T_T) + oG_{EW} \cdot Z_{POC}(T_T) \qquad\qquad D_{BW} = wG_{BW} \cdot Z_W(T_T) + oG_{BW} \cdot Z_{POC}(T_T)$$

DESCRIPTION OF SEDIMENT BURIAL

Sediment burial is treated like an advective transport process using the POC burial rate calculated within the POC budget calculation and the Z-value for POC:

$$D_{LS} = oG_{Wbur} \cdot Z_{POC}(T_W) \qquad\qquad D_{LL} = oG_{Cbur} \cdot Z_{POC}(T_C)$$

4.2.2 Description of Water-Sediment Exchange

Three processes are assumed to contribute to the exchange of contaminants across the water-sediment interface in fresh water and coastal water systems, namely:

- molecular diffusion in the aqueous phase

- bioturbation

- physical sedimentation and resuspension of particulate organic matter

All three processes act in either direction. Diffusion in the aqueous phase is described with the help of a diffusive mass transfer coefficient U_8, which can be interpreted as the ratio of the diffusivity in water B_W and a diffusion path length (calculated as log mean depth of the sediment compartment depth).

$$U_{8S} = B_W \cdot \frac{(1 - VF_{SS})^{1.5}}{0.390865 \cdot h_S} \qquad\qquad U_{8L} = B_W \cdot \frac{(1 - VF_{SL})^{1.5}}{0.390865 \cdot h_L}$$

Bioturbation is treated as a pseudo-diffusive process invoking an equivalent "bioturbation diffusivity" B_{bio}.

$$U_{8Sbio} = \frac{B_{bio}}{0.390865 \cdot h_S} \qquad\qquad U_{8Lbio} = \frac{B_{bio}}{0.390865 \cdot h_L}$$

Finally, sedimentation and resuspension is described as an advective transport process using the particulate organic carbon transport rates in m^3/h derived in the POC balance calculation. The total water sediment D-values thus are:

$$D_{WS} = A_S \cdot U_{8S} \cdot Z_W(T_W) + A_S \cdot U_{8Sbio} \cdot Z_{POC}(T_W) + oG_{Wsed} \cdot Z_{POC}(T_W)$$

$$D_{SW} = A_S \cdot U_{8S} \cdot Z_W(T_W) + A_S \cdot U_{8Sbio} \cdot Z_{POC}(T_W) + oG_{Wres} \cdot Z_{POC}(T_W)$$

$$D_{CL} = A_L \cdot U_{8L} \cdot Z_W(T_C) + A_L \cdot U_{8Lbio} \cdot Z_{POC}(T_C) + oG_{Csed} \cdot Z_{POC}(T_C)$$

$$D_{LC} = A_L \cdot U_{8L} \cdot Z_W(T_C) + A_L \cdot U_{8Lbio} \cdot Z_{POC}(T_C) + oG_{Cres} \cdot Z_{POC}(T_C)$$

4.2.3 Description of Air-Water Exchange

Diffusive air-water exchange is calculated based on the standard two-film theory (Liss and Slater, 1974, Mackay and Leinonen, 1975) invoking two mass transfer coefficients in series, U_1 (in m/h) for the stagnant atmospheric boundary layer and U_2 (in m/h) for the stagnant water layer close to the air-water interface. These mass transfer coefficients are calculated as a functions of wind speed WS using relationships by Mackay and Yuen (1983) as quoted in Schwarzenbach et al. (1993).

$$U_1 = 0.065 \cdot (6.1 + 0.63 \cdot WS)^{0.5} \cdot WS \cdot 36$$

$$U_2 = 0.000175 \cdot (6.1 + 0.63 \cdot WS)^{0.5} \cdot WS \cdot 36$$

The D-values for volatilisation from water are then calculated using

$$D_{WA} = \frac{A_W}{\dfrac{1}{U_{1W} \cdot Z_A(T_W)} + \dfrac{1}{U_{2W} \cdot Z_W(T_W)}} \qquad D_{CA} = \frac{A_C}{\dfrac{1}{U_{1C} \cdot Z_A(T_C)} + \dfrac{1}{U_{2C} \cdot Z_W(T_C)}}$$

Transfer from the atmosphere to the water surface can additionally occur by wet deposition and dry particle deposition. Wet deposition is treated as an advective transport process, and the D-value is simply the product of the rain water flow to the water surface wG_{AX} (in m^3/h) and the bulk Z-value of rain BZ_{Rain} (in mol/(Pa·m^3)). No distinction is made between various forms of precipitation, such as snow or hail. The dry deposition with particles is treated conventionally using a dry deposition velocity to the water surface v_{WD-P} (in m/h) and the volume fraction of solids in the atmosphere VF_{SA}.

$$D_{AW} = D_{WA} + A_W \cdot v_{WD-P} \cdot VF_{SA} \cdot Z_Q + wG_{AW} \cdot BZ_{rain}$$

$$D_{AC} = D_{CA} + A_C \cdot v_{CD-P} \cdot VF_{SA} \cdot Z_Q + wG_{AC} \cdot BZ_{rain}$$

Different approaches are used to account for the influence of an ice cover in the fresh and coastal water environment. Diffusive gas exchange between atmosphere and fresh water ceases when the terrestrial air temperature drops below -2 °C, based on the assumption that an impenetrable ice cover is formed. In the marine environment, the D-values for diffusive gas exchange are reduced by the fraction of the water surface, that is ice-covered. This ice covered fraction is calculated as a function of the marine air temperatures T_C. Neither wet deposition, nor dry particle deposition is assumed to be affected by an ice cover.

4.2.4 Description of Air-Forest Canopy-Forest Soil Exchange

Three transport processes involve the forest canopy compartment, namely foliar uptake of chemical from atmosphere, evaporation of chemical from foliage, and transfer of chemical from foliage to soil. Based on the assumption that the POPs are so hydrophobic that root uptake and transport within the plant is negligible, no uptake of chemical from soil is considered.

Foliar uptake from the atmosphere can occur by gaseous uptake, dry particle deposition and wet deposition, whereby gaseous deposition has been identified as the most important pathway of foliar uptake of some SOCs in coniferous trees (Umlauf et al., 1994). Average dry deposition velocities or mass transfer coefficients describing the transport of gases and particles from air to forest canopy, v_{D-G} and v_{D-P} in m/h, are employed (McLachlan and Horstmann, 1998). The gaseous deposition velocity includes stomatal uptake of vapor as well as gas absorption in the cuticle, the latter process being far more significant for hydrophobic chemicals. These gaseous and dry particle-bound deposition velocities undergo a significant seasonal change (Figure 6). Deposition to a deciduous canopy obviously undergoes large changes in time as a result of the seasonality of leaf development. Additionally, mass transfer to the terrestrial surface is often reduced in winter as a result of surface cooling and the absence of solar energy. This creates a more "stable" atmosphere which suppresses turbulence. Horstmann and McLachlan (1998) assumed for example that in Bayreuth, Germany the more stable atmospheric conditions during winter reduce deposition velocities to forests by a factor of three. However, this effect will depend on climatic conditions and may even be <1 in regions with much higher wind speeds during winter than summer.

The seasonal variability in surface mass transfer is taken into account by defining a stability factor, $fac_{Stability}$, which expresses the extent to which the typically more stable winter atmosphere reduces the gaseous mass transfer coefficient over terrestrial surfaces. During summer v_D equals v_{Dmax}, in winter v_D is v_{Dmax} / $fac_{Stability}$, and during spring and fall v_D is interpolated between

winter and summer values (Figure 6). In the case of the deciduous canopy, v_D is additionally reduced by a factor reflecting the fraction of the canopy which stays on the trees during winter. To express volatilization of chemical from the foliage, the same gaseous mass transfer coefficient v_{D-G} as for gaseous uptake is employed.

Wet deposition to the canopy occurs by vapor absorption in rain water and scavenging of particle-sorbed chemical. It is assumed that (1) the intercepted water dripping or flowing from the canopy to the soil has the same chemical concentration (in the dissolved phase and sorbed onto particles) as the original precipitation, and (2) the amount of chemical in the water evaporating from the canopy is negligible. This enables the chemical being scavenged by rain to be split into a fraction taken up by leaves and a fraction being transferred directly to soils, using the fraction of water that is intercepted by the canopy and evaporates from there, frU_F. In summary, the D-values for the exchange between atmosphere and canopy are calculated as follows:

$D_{AF} = A_B \cdot (v_{FD-G} \cdot Z_A(T_T) + v_{FD-P} \cdot VF_{SA} \cdot Z_Q + frU_F \cdot U_{3T} \cdot BZ_{rain})$

$D_{FA} = A_B \cdot v_{FD-G} \cdot Z_A(T_T)$

The transport of contaminant with litter fall is an advective transport process, described as the product of the litter fall rate G_{FB} in m^3 leaves/h and the foliage Z-value. The overall D_{FB} is a weighted fraction of the coniferous and deciduous component.

$D_{FB} = \Phi_{con} \cdot G_{FBcon} \cdot Z_{Fcon} + (1 - \Phi_{con}) \cdot G_{FBdec} \cdot Z_{Fdec}$

4.2.5 Description of Air-Soil Exchange

DIFFUSIVE AIR-SOIL EXCHANGE

In the classical approach to describe diffusive air-soil exchange in multimedia mass balance models (Mackay and Stiver, 1991, Jury et al. 1983), the two-resistances in series model of air water exchange is modified using a resistance in the stagnant air boundary layer over the soil and two parallel resistance to diffusion within the soil. We adopt a nomenclature of U_7 for the mass transfer coefficient through the atmospheric boundary layer, U_5 for diffusion in the air pore space and U_6 in the water-filled pore space. The D-value for evaporation of chemical from soil then is:

$$D_{BA} = \cfrac{A_B}{\cfrac{1}{U_{7B} \cdot Z_A(T_T)} + \cfrac{1}{U_{5B} \cdot Z_A(T_T) + U_{6B} \cdot Z_W(T_T)}}$$

with an analogous equation for D_{EA}.

The reduced atmospheric turbulence under a forest canopy is likely to lead to a reduction in the gaseous deposition velocities to the forest soil surface when compared to an open soil surface. CoZMo-POP thus allows for different values of U_{7E} and U_{7B} over agricultural soils and forest soils. The atmospheric stability differences between summer and winter discussed above are taken into account employing the stability factor, $fac_{Stability}$. During summer U_7 equals U_{7max}, in winter U_7 is $U_{7max} / fac_{Stability}$, and during spring and fall U_7 is interpolated between winter and summer values.

Diffusion in soil water/soil air is modelled using a modification of the classical approach by Jury et al. (1983, 1984). The mass transfer coefficients for diffusion in the soil pore space U_5 and in the water-filled pore space U_6 are calculated using the molecular diffusion coefficients in air B_A and water B_W. These coefficients are relatively constant for POPs, and the values chosen by Jury et al. (1984) are used (0.018 and 0.0000018 $m^2 \cdot h^{-1}$, respectively). The diffusion path length

in soil is taken as the log mean depth of the soil compartment, corrected for tortuosity using the Millington-Quirk formula:

$$U_{5B} = \frac{B_A \cdot \dfrac{VF_{AB}^{10/3}}{(VF_{AB} + VF_{WB})^2}}{0.390865 \cdot h_B} \qquad\qquad U_{6B} = \frac{B_W \cdot \dfrac{VF_{WB}^{10/3}}{(VF_{AB} + VF_{WB})^2}}{0.390865 \cdot h_B}$$

Equivalent equations apply for U_{5E} and U_{6E}.

This classical approach is not applicable to the soil/air exchange of POPs, since it does not address processes such as bioturbation or ploughing that control the transport of chemicals with very low mobility in the soil column. As an interim solution it is proposed that a minimum value for the mass transfer coefficient k_S for transport within the soil be specified, based on estimates of the transport of solids in bulk soils.

In CoZMo-POP k_S equals $(U_5 \cdot Z_A(T_T) + U_6 \cdot Z_W(T_T)) / (VF_{OB} \cdot Z_{POC}(T_T))$.

If therefore $U_5 \cdot Z_A(T_T) + U_6 \cdot Z_W(T_T)$ is smaller than $(VF_{OB} \cdot Z_{POC}(T_T)) \cdot k_{Smin}$, where k_{Smin} is the specified threshold for the diffusion in soil MTC, the D-value for soil to air diffusion is calculated using:

$$D_{BA} = \frac{A_B}{\dfrac{1}{U_7 \cdot Z_A(T_T)} + \dfrac{1}{VF_O \cdot Z_{POC}(T_T) \cdot k_{Smin}}}$$

OTHER DEPOSITION PROCESSES TO SOIL

Transport of POPs to the soils by dry particle and wet deposition is treated like these processes over water. The D-values for air-soil exchange therefore are:

$D_{AE} = D_{EA} + A_E \cdot v_{ED-P} \cdot VF_{SA} \cdot Z_Q + wG_{AE} \cdot BZ_{rain}$

$D_{AB} = D_{BA} + A_B \cdot v_{BD-P} \cdot VF_{SA} \cdot Z_Q + wG_{FB} \cdot BZ_{RAIN}$

Similar to the dry particle deposition velocities to the forest canopies, the dry deposition velocities to soils v_{ED-P} and v_{BD-P} are a function of season as shown in Figure 6. Again, different dry particle deposition velocities to agricultural and forest soil v_{ED-P} and v_{BD-P} can be defined to account for the interception of particles by the canopy and the reduced atmospheric turbulence in the forest.

4.2.6 Description of Degradation Processes

D-values for degradation processes in fugacity terms are calculated as the product of a Z-value, the compartment volume and a first-order degradation rate k in units of h^{-1}. In CoZMo-POP all degradation rates are calculated as function of compartment temperature.

DESCRIPTION OF ATMOSPHERIC DEGRADATION

The reaction of the chemical in the gas phase with hydroxyl radicals is assumed to be the only significant degradation pathway for POPs in the atmosphere (Atkinson, 1996). The degradation rate k_{RA} is calculated as a function of seasonally variable atmospheric OH radical concentrations [OH] and temperatures T_A, requiring a contaminant-specific degradation rate k_{RAref} at the reference temperature 25°C and an activation energy A_{EA}.

$k_{RA} = k_{RAref} \cdot [OH] \cdot 3600 \text{ s/h} \cdot Exp(A_{EA} / R \cdot (1 / 298.15 - 1 / T_A))$

The D-value is calculated using this reaction rate constant and the gas phase Z-value only:

$D_{RA} = k_{RA} \cdot V_A \cdot Z_A$

DEGRADATION IN OTHER MEDIA

Degradation rates in other compartments are calculated as a function of temperature using a contaminant-specific degradation rate k_{RXref} at the reference temperature 25°C and an activation energy A_{EX}. This degradation rate is assumed to include all degradation processes that the POP can undergo, including biodegradation, hydrolysis, and photolysis.

$k_{RX} = k_{RXref} \cdot Exp(A_{EX} / R \cdot (1 / 298.15 - 1 / T_X))$

Assuming that the degradation proceeds in all sub-phases of a compartment at the same rate, the D-values are calculated using the bulk-phase Z-values:

$D_{RX} = k_{RX} \cdot V_X \cdot BZ_X$

4.2.7 Description of Emissions and Boundary Conditions in CoZMo-POP

The model is non-steady state and driven by historical emission estimates and the inflow of contaminated air and water across the model boundaries. It allows the user to define chemical-specific emission scenarios by reading annual emission rates from file and then modifying these rates according to mode of emission and seasonality.

Emission is allowed to occur into all types of compartments, except the sediments. The default assumption is that all emission occurs into the atmosphere. The user can specify fractions, which distribute the annual emission rate among the compartments air, forest canopy, forest soil, agricultural soil, fresh water and coastal water. Obviously, these fractions have to add up to one. These fractions are assumed fixed in time.

The default assumption is that the annual emissions are distributed evenly across the entire year. However, it is possible to modulate this by superimposing a sinusoidal function on the emission rates. The user can specify the amplitude (as a fraction of the mean) and the month of maximum emission. Again, these parameters are fixed from year to year.

Finally, the model allows the user to specify a time-invariant scaling factor, which facilitates the modellling of contaminant mixtures. If the annual release rates is for a mixture of POPs (e.g. an Aroclor mixture), the scaling factor could be the fraction of that mixture, which is a certain constituent (e.g. a PCB congener or homologue).

In the model time variant emission rates E_X into six compartments in units of mol/h are calculated, which are parameters in the mass balance equations (Table 3).

BOUNDARY CONDITIONS

POPs enter the modelled region with air and sea water advected into the region. The user may specify time invariant fugacity values in these incoming media, including the option to assume fugacities of 0 Pa, which implies no import of chemical from outside of the region. However, often the concentration in these media is not very well established, certainly not in a historical perspective. This is why the model allows the user to specify ratios Rf_A and Rf_C that relate the fugacity in the incoming flow with the calculated fugacity in the compartment receiving the inflow of air or water.

$f_{Aut} = f_A \cdot Rf_A$

$f_O = f_C \cdot Rf_C$

If these ratios are one, the system boundary acts like an inert wall returning just as much chemical into the drainage basin as has left by outbound advection (assuming similar

temperature and phase composition i.e. VF_{SA} and $Cpoc_O$, inside and outside of the model region). A ratio greater than one implies a net import of contaminant, a ratio smaller than one a net outflow. These ratios may be estimated based on information of the relative magnitude of measured concentrations or estimated emissions on either side of the system boundary.

5 The Default Environmental Input Parameter

Table 3 gives the default values for the environmental input parameters, which are constant in time, whereas Figure 7 displays the default values for temperature, and the hydroxyl radical concentration. The resultant water mass balance is shown in Figure 8, the POC balance in Figure 9.

Table 3   Default values for the environmental input parameters.

		drainage	coastal
$A_{T,C}$	Surface area of the basin in km^2	80,000	20,000
$U3_{T/C}$	Rain rate over basin in cm/a	70	70
$WS_{T/C}$	Wind speed over basin in m/s	5	6
FrtARW	Fraction of the drainage basin covered by fresh water	0.05	
frtARB	Forest covered fraction of the terrestrial systems	0.50	

Atmospheric Parameters

VF_{SA}	Volume fraction of aerosols in m^3 solids /m^3 air	$1 \cdot 10^{11}$
h_A	Average atmospheric height in km	2
T_A	Atmospheric residence time in hours	48
Q	Particle scavenging ratio	68000
$Fac_{Stability}$	Stability of winter atmosphere relative to summer conditions	3
M_Q / N_Q	Regression parameter for $K_{QA} = M_Q \cdot K_{OA}^{NQ}$	3.5 / 1

Soil Parameters

		forest	agriculture
$h_{B/E}$	Average soil depth in m	0.1	0.2
$VF_{AB/E}$	Volume fraction of air in soil	0.25	0.25
$VF_{WB/E}$	Volume fraction of water in soil	0.25	0.25
$VF_{SB/E}$	Volume fraction of suspended solids in soil run-off water	0.0001	0.0005
$OC_{B/E}$	Organic carbon mass fraction of soil solids	0.02	0.02
$frU_{B/E}$	Evaporation loss from soil	0.25	0.60
$U7_{B/E}$	MTC through air boundary layer over soil in m/h	0.416	2.08
$k_{SminB/E}$	Minimum MTC within soil in m/a	0.005	0.01
$v_{B/ED-P}$	Maximum dry particle deposition to soils in m/h	0.206	1.03
M_{POC}	Regression parameter for $K_{POC} = M_{POC} \cdot K_{OW}$	0.41	0.41

Table 3 continued   Default values for the environmental input parameters.

Water Parameters

		fresh	coastal
$h_{W/C}$	Average water depth in m	2	20
$h_{S/L}$	Surficial sediment depth in m	0.05	0.05
$frU_{W/C}$	Evaporation loss from water compartments (fraction of input)	0.20	1.00[2]
$Cpoc_{W/C}$	Concentration of POC in water in mg/L	5	1
$OC_{S/L}$	Mass fraction organic carbon in sediments	0.03	0.03
$BP_{W/C}$	Primary productivity in g C/(m^2·a)	100	250
$facO_{W/Cmiw}$	Mineralisation intensity in water column	0.85	0.8
$facO_{W/Cres}$	Resuspension intensity	0.75	0.5
$facO_{W/Cmis}$	Mineralisation intensity in surface sediments	0.75	0.75
$VF_{SS/L}$	Volume fraction of solids in surface sediment	0.30	0.30
$B_{bioS/L}$	Bioturbation diffusivity in m^2/h	10^{-10}	10^{-10}
$frcAR_{S/L}$	Sediment focussing factor	1.00	0.33
$v_{W/CD-P}$	Dry deposition velocity to water in m/h	1.03	1.03
M_{POC}	Regression parameter for $K_{POC} = M_{POC} \cdot K_{OW}$	0.41	0.41

Forest Canopy Parameters

		coniferous	deciduous
Φ_{con}	Fraction of the forest made up from coniferous trees	0.50	
frU_F	Evaporation loss from forest canopy (fraction of input)	0.35	
v_{FD-P}	Maximum dry particle deposition velocity to canopy in m/h	0.7+2.7[1]	0.7+26.3[1]
v_{FD-G}	Maximum dry gaseous deposition velocity to canopy in m/h	42.1[1]	130[1]
$sV_{Fcon/dec}$	Specific canopy volume in m^3/m^2	0.0017	0.0012[1]
M_F / N_F	Regression parameter for $K_{FA} = M_F \cdot K_{OA}^{NF}$	38 / 0.69	14 / 0.76
frcLeaf	Fraction of canopy, which stays on trees during winter in %		10
t_{Needle}	Average life time of needles in years	5	

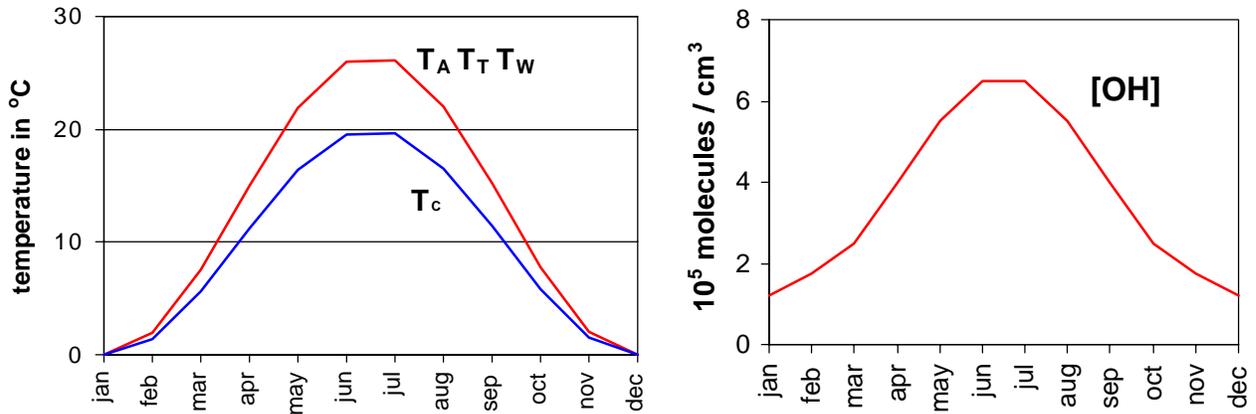[1] summer average, [2] no net water exchange with open sea

Figure 7 Default values for the environmental temperatures and the OH radical concentration in the atmosphere. The temperatures in the atmosphere, in the terrestrial environment and in the fresh water system are assumed to be the same.
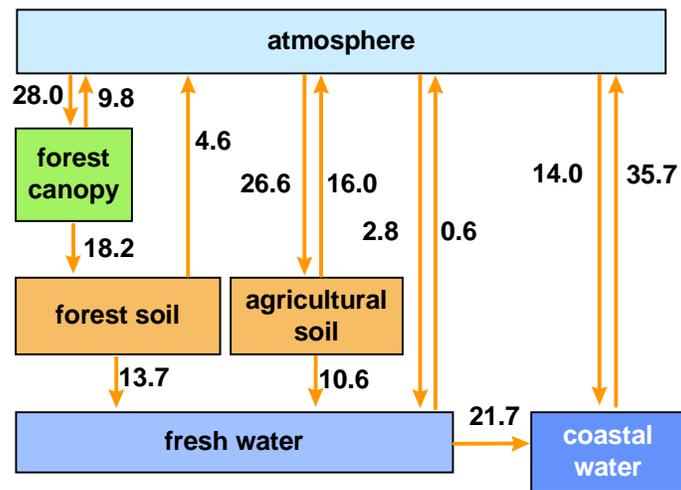

Figure 8 Water balance in km^3/a calculated from the default input parameters.
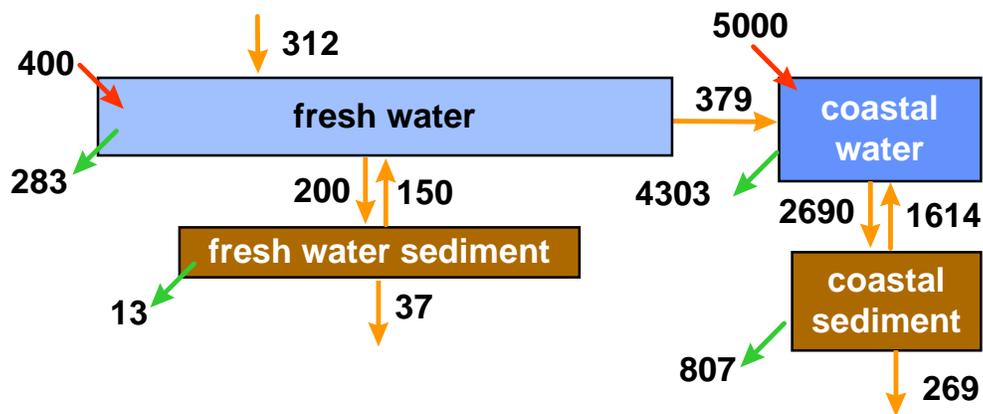

Figure 9 POC balance in kt/a calculated from the default input parameters.

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Appendix 1: Glossary

Environmental Properties

Compartment dimensions

A_X surface area of compartment X in m^2
h_X depth of compartment X in m
V_X volume of compartment X in m^3

Volume fractions in m^3/m^3

VF_{SA} volume fraction of aerosols in atmosphere
VF_{conF} volume fraction of coniferous foliage in forest canopy compartment
VF_{SS} volume fraction of solids in sediment (equivalent for VF_{SL} and VF_{SM})
VF_{OS} volume fraction of organic carbon in sediment solids
VF_{WE} volume fraction of water in agricultural soil
VF_{AE} volume fraction of air in agricultural soil
VF_{OE} volume fraction of organic carbon in agricultural soil solids
VF_{WB} volume fraction of water in forest soil
VF_{AB} volume fraction of air in forest soil
VF_{OB} volume fraction of organic carbon in forest soil solids

$Cpoc_X$ concentration of POC in water compartment X in units of g/m^3
OC_X mass fraction organic carbon in solids of compartment X

δ_{OC} density of organic carbon in g/m^3
δ_{MM} density of mineral matter in g/m^3

[OH] OH radical concentration is in units of molecules/cm^3

T_A atmospheric temperature in K
T_W temperature of fresh water in K
T_T temperature of terrestrial environment in K

R ideal gas constant in units of J/(K·mol)

Transport Parameters

Q particle scavenging ratio (dimensionless)

Diffusivities in m^2/h

B_W molecular diffusivity in air in m^2/h
B_A molecular diffusivity in water in m^2/h
B_{bio} bioturbation diffusivity in units of m^2/h

Mass transfer coefficients in m/h

U_1 mass tranfer coefficient for the stagnant atmospheric boundary layer over water in m/h
U_2 mass transfer coefficient for the stagnant water layer at the air-water interface in m/h
v_{FD-G} gaseous deposition velocity to the forest canopy in m/h
v_{FD-P} particle deposition velocity to the forest canopy in m/h

v_{ED-P} particle deposition velocity to the agricultural soil in m/h
v_{BD-P} particle deposition velocity to the forest soil in m/h
v_{WD-P} particle deposition velocity to a water surface in m/h
U_8 mass transfer coefficient for diffusion across the air-sediment interface in m/h
U_{8bio} mass transfer coefficient for bioturbation in m/h

wG_{XY} water advection rates from compartment X to compartment Y in units of m3/h

wG_{AF} precipitation to canopy
wG_{FA} evaporation from canopy
wG_{FB} throughfall/stem flow
wG_{BA} evaporation from forest soil
wG_{BW} run-off/leaching from forest soil
wG_{AE} precipitation to agricultural soil
wG_{EA} evaporation from agricultural soil
wG_{EW} run-off/leaching from agricultural soil
wG_{AW} precipitation to fresh water
wG_{WA} evaporation from fresh water
wG_{WC} riverine run-off
facGF factor by which fresh water flux between coastal and open water is increased by marine inflow

frU_X fraction of precipitation to a compartment that evaporates from that compartment

oG_X flux or rate of POC within aquatic system X in units of m^3 POC/h

(X = W for fresh water, C for coastal water)
oG_{Xpro} primary production of POC within system
oG_{Xmiw} POC mineralisation in the water column
oG_{Xsed} POC settling to the sediments
oG_{Xres} POC resuspension from sediments
oG_{Xmis} POC mineralisation in surface sediment
oG_{Xbur} POC sediment burial

oG_{EW} run-off of POC from agricultural soil to fresh water
oG_{BW} run-off of POC from forest soil to fresh water
oG_{WC} run-off of POC from fresh water to coastal water

Other advective transfer rates in m^3/h

aG air advection rate
G_{FB} litter fall term in m^3 leaves/h

Chemical Properties

H Henry's law constant in Pa·mol/m^3
K_{OW} octanol-water partition coefficient (dimensionless)
K_{OA} octanol-air partition coefficient (dimensionless)
K_{POC} partition coefficient between particulate organic carbon and water (dimensionless)
K_{FA} foliage-air partition coefficient (dimensionless)
k_{RA} reaction rate in air in units of h^{-1}
k_{RAref} reaction rate in air at 25°C in units of cm^3/(molecules·s)
A_{EA} activation energy of the reaction with OH radicals in J/mol
k_{RX} reaction rate in phase X in units of h^{-1}
k_{RXref} reaction rate in phase X at 25°C in units of h^{-1}

A_{EX} activation energy of the degradation reaction in J/mol

f_X fugacity in compartment X in Pa

Z-values in mol/($m^3 \cdot Pa$)

Z_A Z-value for pure air
Z_W Z-value of water
Z_{POC} Z-value of particulate organic carbon
Z_Q Z-value for the aerosol phase
Z_{Fdec} Z-value for deciduous forest canopy
Z_{Fcon} Z-value for coniferous forest canopy

BZ_X bulk Z-value of compartment X
BZ_{rain} bulk Z-value of rain water
BZ_F bulk Z-value for forest canopy (foliage)

D-Values in units of mol/($h \cdot Pa$)

D_{AF} D-value for air to forest canopy transfer
D_{AB} D-value for air to forest soil transfer
D_{AE} D-value for air to agricultural soil transfer
D_{AW} D-value for air to fresh water transfer
D_{AC} D-value for air to coastal water transfer
D_{FA} D-value for forest canopy to air transfer
D_{BA} D-value for forest soil to air transfer
D_{EA} D-value for agricultural soil to air transfer
D_{WA} D-value for fresh water to air transfer
D_{CA} D-value for coastal water to air transfer
D_{FB} D-value for forest canopy to forest soil transfer
D_{BW} D-value for forest soil to fresh water transfer
D_{EW} D-value for agricultural soil to fresh water transfer
D_{WS} D-value for fresh water to sediment transfer
D_{SW} D-value for sediment to fresh water transfer
D_{CL} D-value for coastal water to sediment transfer
D_{LC} D-value for sediment to coastal water transfer
D_{LS} D-value for fresh water sediment burial
D_{LL} D-value for coastal sediment burial
D_{CO} D-value for coastal water to open water transfer
D_{OC} D-value for open water to coastal water transfer
D_{Ain} D-value for atmospheric advection into the model region
D_{Aut} D-value for atmospheric advection out of the model region
D_{RX} D-value for degradation loss from compartment X